



## Short communication

# Determining the platinum loading and distribution of industrial scale polymer electrolyte membrane fuel cell electrodes using low energy X-ray imaging

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## H I G H L I G H T S

- Low energy X-ray imaging evaluated as a tool for non-destructive characterization of electrodes.
- Linear correlation between image grayscale and platinum loading observed.
- Platinum distribution mapping across electrode area implemented.
- Resolution sufficient to identify flaw and inhomogeneity of industrial electrode fabrication.

## A R T I C L E I N F O

## Article history:

Received 18 May 2014

Received in revised form

4 July 2014

Accepted 14 July 2014

Available online 24 July 2014

## Keywords:

Fuel cells

Catalyst distribution

X-ray imaging

Catalyst layer

## A B S T R A C T

Low energy X-ray imaging ( $E < 25$  keV) is herein demonstrated to be a rapid, effective and non-destructive tool for the quantitative determination of the platinum loading and distribution over the entire geometric area of gas diffusion electrodes for polymer electrolyte membrane fuel cells. A linear correlation was found in order for the average image grayscale intensity to be calibrated to the platinum loading, while the platinum distribution was mapped across the electrode geometric area. The resolution was found to be sufficient in identifying flaws and inhomogeneities in the catalyst layer of electrodes fabricated using an industrial spraying process. This technique proves to be an attractive option for the electrode performance study, the process optimization and quality control of electrode fabrication on an industrial scale.

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## 1. Introduction

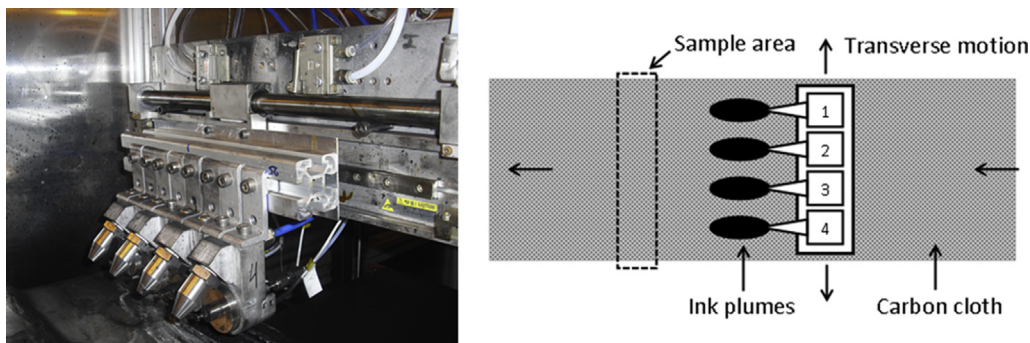
Polymer electrolyte membrane (PEM) fuel cells are an energy conversion technology with advantages including low startup times, light weight, and high electrochemical conversion efficiencies [1]. The potential applications range from vehicular propulsion, stationary power generation and portable power sources. The core of such a cell consists of either an acid-based or alkaline-based polymeric membrane such as Nafion<sup>®</sup> [2], phosphoric acid-doped polybenzimidazole [3], or a poly(ethylene-co-tetrafluoroethylene)-derived radiation-grafted anion-exchange membrane [4]. On each side of the membrane are attached two thin gas diffusion electrodes. The electrodes contain a catalyst material deposited onto a macro-porous carbon fiber-based gas diffusion

layer (GDL) to form a thin, micro-porous catalyst layer (CL) that is in intimate contact with the PEM [5]. In acidic conditions, Pt and noble metal alloys have been shown to exhibit the most promising catalytic activity of all materials at either electrode, and have thus been intensively investigated over the last few decades [6].

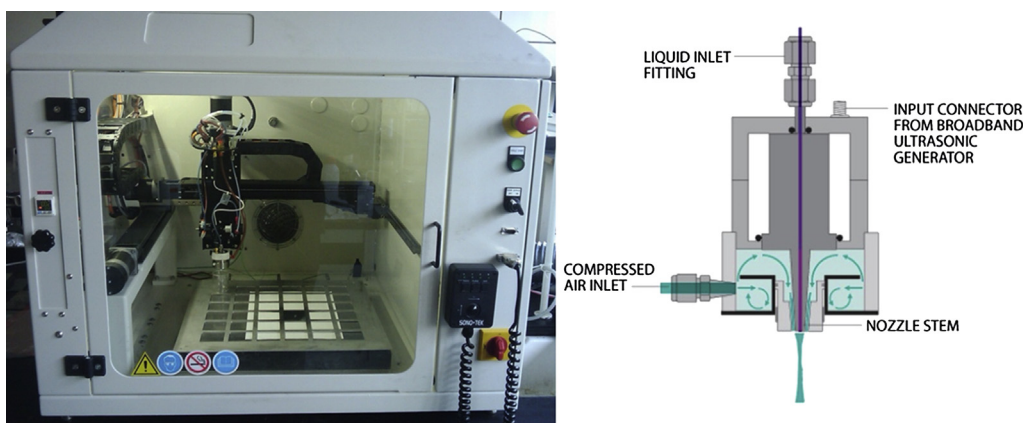
In order to achieve a low cost on the production of MEAs in commercial quantities, it is necessary to develop processes for the efficient deposition of the CL onto the GDL. A fast, effective and non-destructive method to determine the catalyst loading and distribution on the resultant electrode is a key to characterizing the electrodes with a view to optimizing the process. In laboratory practice, where electrode fabrication is often carried out on a few square centimeters in size and a couple of electrodes of a batch, the catalyst loading on the resultant electrodes is often determined by gravimetrically measuring the accumulated weight of the GDL after spraying. This method gives no information regarding the catalyst distribution. Relating MEA performance to variations in the Pt loading thereby assumes a uniform CL thickness across the

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**Fig. 1.** A photo of the 4-nozzle spraying equipment with its operation shown schematically on the right, indicating the belt motion and the transverse motion of the spray nozzles.



**Fig. 2.** (left) A photo of the Exacta-Coat spray robot used to prepare Pt–Ru coated carbon cloth electrodes, (right) schematic of the ultrasonic nozzle used to spray the electrodes.

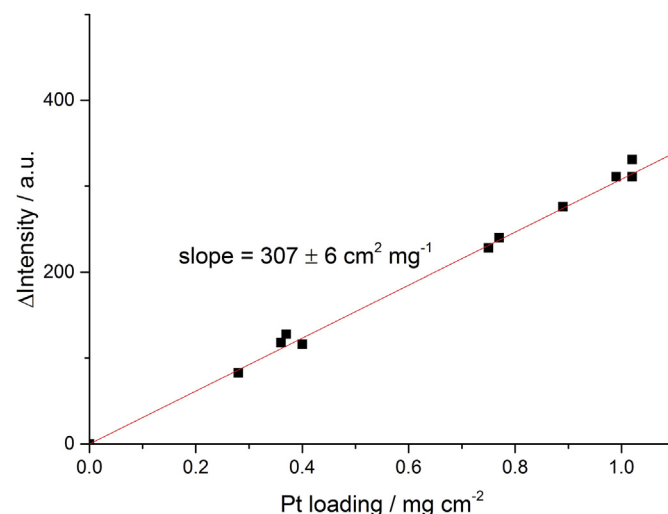
electrode. Other characterization tools such as energy-dispersive X-ray spectroscopy (EDS), secondary electron imaging (SEI), transmission electron microscopy (TEM), X-ray diffraction (XRD), and Raman spectroscopy are seldom used in the electrode characterization particularly when large-area electrodes of industrial scale are concerned. Furthermore, high-resolution X-ray computed tomography and absorption edge imaging techniques have recently been developed to investigate the local morphology and chemistry of fuel cell components at a nanometer-scale resolution during operation [7–15]. The commercialization and high-volume manufacturing of MEAs will ultimately require that certain quality control measures be devised to ensure that the catalyst deposition process – the most critical step in the production of a fuel cell – is reliable.

Low energy X-ray imaging ( $E < 25$  keV) is an established technology that has been used extensively in high-volume areas such as quality control and border security. Currently, X-ray imaging units are sold worldwide as stand-alone units or can be tailored for in-line integration. In this communication we report the first evaluation process and calibration of the low energy X-ray imaging as a technique for simultaneous measurement of the loading and geometric area distribution of Pt on PEMFC gas diffusion electrodes with a throughput suited to large-scale processes.

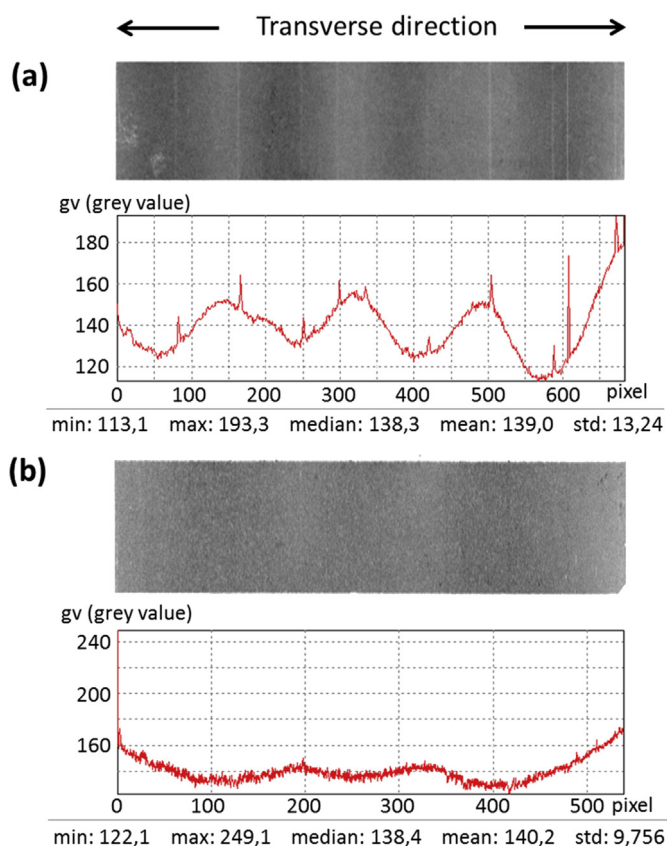
## 2. Experimental

Two techniques were used to fabricate large scale electrodes with tailored platinum loadings for the evaluation and calibration of the low energy X-ray imaging. The first technique is based on a custom-built spray coater (Danish Power Systems) with four

ultrasonic nozzles that was used to spray a Pt/C-based catalyst ink onto a 20 cm wide rotating carbon cloth belt, as shown in Fig. 1. Catalytic inks were fed at a constant flow rate to the nozzles, which have the ability to oscillate in the transverse direction at user-defined speeds and amplitudes. The catalytic inks consisted of either a proprietary Pt/C (Danish Power Systems) or Pt–Ru/C formulations using formic acid as the solvent. The second technique of electrode preparation was carried out using a spray robot, Exacta-



**Fig. 3.** A plot of the average Pt loading versus the difference in average grayscale intensity between that of platinized carbon cloth and bare carbon cloth.



**Fig. 4.** Low energy X-ray images of 5 cm wide strips taken from different belts sprayed with (a) stationary nozzles, and (b) moving nozzles with a transverse displacement of 2.9 cm. Shown below each image is a plot of the grayscale intensity versus the transverse position was made using *Isee!* software package.

Coat from SONO-TEK Corporation, which consists of a programmable 3-axis system fitted with a single Accumist ultrasonic nozzle (see Fig. 2). The spraying was performed using an alternating serpentine nozzle path. Low energy X-ray ( $E < 25$  keV) measurements were taken of sample areas using an Innospexion X-ray

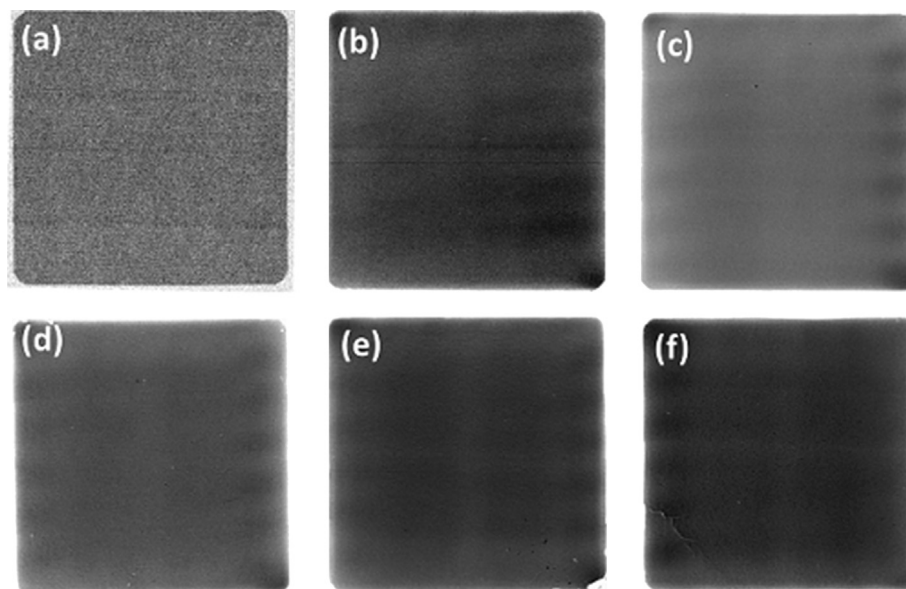
measurement system. Image software (*Isee!* from BAM) was used to analyze the grayscale images.

### 3. Results and discussion

The contrast in the low energy X-ray image is the result of attenuation of the X-rays by electron density in the beam path thereby lowering the intensity of X-rays at the detector. This technique is thus particularly sensitive to changes in the Pt loading of the electrode. A sub-millimeter spatial image resolution is comfortably achieved as to aid in the detection and mapping of any coating artifacts. The *Isee!* software package has an inbuilt function that calculates the average grayscale value for a given 2D image.

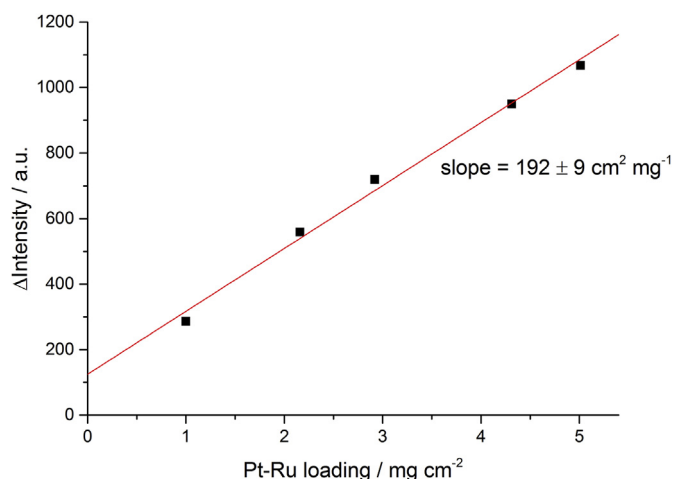
A calibration curve that relates the average grayscale intensity of a given electrode image to its platinum loading was constructed by taking images of several electrodes with varying platinum loadings (as determined gravimetrically). The *Isee!* software package allows the brightness and contrast of the X-ray images to be manually adjusted in order for each image to best exhibit the variations in platinum loading across the electrode. In preparing the calibration curve, care was taken to ensure that the contrast and brightness settings remained constant for a given set of samples. Under the selected brightness and contrast settings, the average grayscale value of an unsprayed piece of carbon cloth was 195 arbitrary units. This value is taken as the reference from which the measurements on the platinized carbon cloth samples are subtracted. Fig. 3 shows that, in the studied platinum loading range from 0.28 to  $1.0 \text{ mg cm}^{-2}$ , the difference in average grayscale value ( $\Delta\text{intensity}$ ) varies linearly with the average loading of Pt electrodes prepared using the 4-nozzle spray coater. For further lower Pt loadings below  $0.2 \text{ mg cm}^{-2}$ , however, no data was obtained in the present study as an issue arises during the gravimetric calibration. The absolute loading of Pt on a given electrode sample can thus be determined in a non-destructive and rapid process.

The distribution of Pt over the geometric area of the electrode is further analyzed by plotting the grayscale value along the transverse direction after deposition, as shown in Fig. 4a. In this case, the spray nozzles remained stationary during spraying so that the regions with the highest Pt loading appear as four distinct minima corresponding to the positions of each of the spray nozzles. For the



**Fig. 5.** Low energy X-ray images of  $5 \text{ cm} \times 5 \text{ cm}$  electrodes printed using an Exacta-Coat from SONO-TEK Corporation spray robot. 60 wt% Pt–Ru on carbon was deposited using a serpentine spray pattern to loadings of (a) pristine carbon cloth, (b)  $1.0 \text{ mg cm}^{-2}$ , (c)  $2.1 \text{ mg cm}^{-2}$ , (d)  $2.9 \text{ mg cm}^{-2}$ , (e)  $4.3 \text{ mg cm}^{-2}$ , and (f)  $5.0 \text{ mg cm}^{-2}$ .





**Fig. 6.** A plot of average grayscale intensity versus the gravimetrically determined Pt–Ru loading.

purposes of clarity, the average grayscale intensity of the bare carbon cloth (195) is set as the maximum y-value in Fig. 4. The difference between Pt-rich ( $gv \approx 130$ ) and Pt-poor ( $gv \approx 155$ ) represents a significant Pt variation with a peak–peak amplitude of approximately 35 grayscale units, or 50%, along the direction transverse to the belt motion.

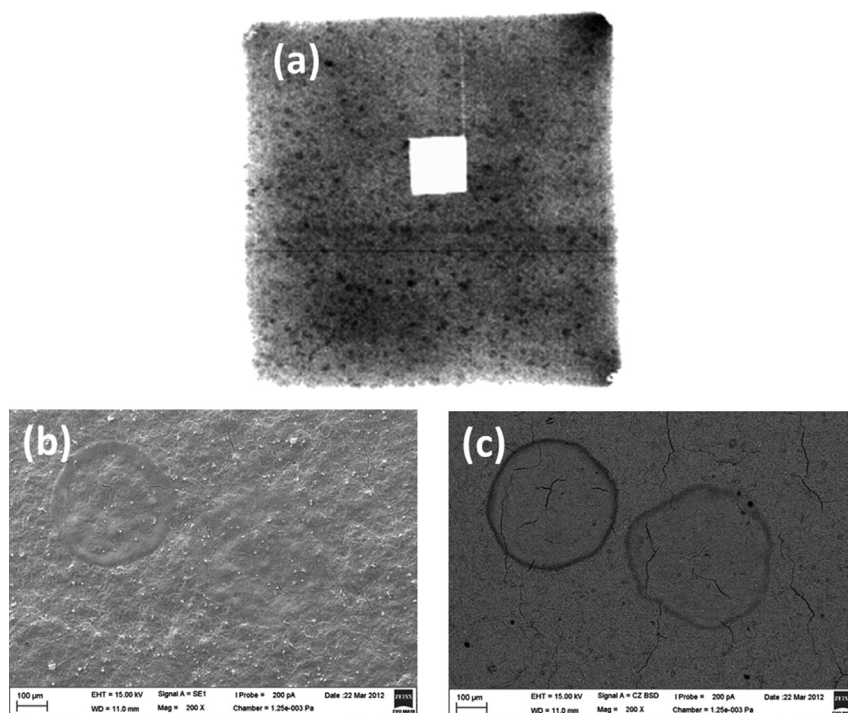
The application of a transverse motion to the spray nozzles is common practice in industrial electrode catalyst spraying processes. Optimization of the relative positioning and movement of the nozzles is required in order to achieve uniform Pt loadings over a greater electrode area. For those electrodes in Fig. 4b, this aspect was introduced into the spraying process with a transverse displacement amplitude of 2.9 cm. It is important to note that the grayscale brightness and contrast were adjusted for this set of

measurements so that the bare carbon cloth gave an average grayscale intensity of 245. It is immediately apparent that the amplitude of the grayscale variations is significantly lower, indicating a more uniform Pt coverage across the electrode surface. The peak–peak amplitude of approximately 40 grayscale units represents a variation of 15 wt% – less than one third of that recorded for stationary nozzles.

Another benefit of this imaging technique is the ability to quantify the drop in the Pt loading towards the edges of the sprayed electrode area. Doing so with such precision is of particular value in an effort to minimize the amount of discarded electrode. It is thus demonstrated that this technique is useful for rapid feedback on the uniformity and Pt loading of the deposited CL.

This X-ray imaging technique was also used to investigate the catalyst layer homogeneity on electrodes prepared from the spray robot. The electrodes were prepared using an electrocatalytic ink containing Pt–Ru (60 wt% on carbon black) and a low level of phosphoric acid as to assist with operation in a phosphoric acid-doped polybenzimidazole high-temperature PEM fuel cell setup [16,17]. Fig. 5 shows the low energy X-ray images of the pristine GDL (Fig. 5a) in addition to electrodes with Pt–Ru loadings in the range of 1–5 mg cm<sup>-2</sup>. The brightness and contrast of each image was manually optimized to give the clearest visual indication of the catalyst distribution, hence the increase in the overall grayscale intensity does not appear to correspond to the increase in catalyst loading. It can be seen from the images that the catalyst is relatively well distributed over the electrode surface, although more catalyst is present along the turns of the serpentine curve (next to the electrode edges). The instances where low loadings occur on the corners may be due to the GDL not lying completely flat in the mask. The crack on electrode (f) was also visible with the naked eye.

A calibration curve for these electrodes, similar to that presented in Fig. 3, was prepared by first adjusting the brightness and contrast of the images in Fig. 5 to a constant level. Fig. 6 shows the linear relationship between the average grayscale intensity and the



**Fig. 7.** (a) Low energy X-ray image of a Pt/C (0.65 mg cm<sup>-2</sup>) electrode prepared using the Exacta-Coat spray robot, (b) secondary electron image of the same electrode, and (c) a backscattered electron image of the same location as (b).

catalyst loadings. The standard deviation from the average grayscale intensity over the entire electrode surface is approximately  $\pm 20$  grayscale units for each electrode. These variations are similar to those seen for the 4-nozzle system with transverse motion (15%). The trendline in Fig. 6 does not pass through the origin due to the cumulative X-ray attenuation attributed to the fixed content of phosphoric acid that is present in these electrodes. It can thus be expected that the added phosphoric acid would shift the trendline in the positive y-direction, as is observed. No further study on the phosphoric acid calibration, however, was made in the present work.

The ability of low energy X-ray imaging to identify spray patterns and features on the electrode surface is demonstrated in Fig. 7. Here, the X-ray image for an electrode with  $0.65 \text{ mg cm}^{-2}$  of Pt deposited reveals a Pt distribution that contains fine millimeter-scale features across the whole electrode. The secondary electron image in Fig. 7b confirms the presence of droplet formations on the electrode surface, with the backscattered electron image in Fig. 7c suggesting that these features are present within multiple coatings of the catalyst layer. In this case, it is reasoned that the inhomogeneity of the ink results in temporary blockages of the spray nozzle. The subsequent release of the accumulated material forms large ink droplets that, upon drying, deposit more Pt along the circumference of the droplet/electrode boundary.

It is thereby demonstrated that this technique provides valuable information regarding not only the platinum loading and distribution of the catalyst layer, but also on flaws and imperfections on the sub-millimeter scale that originate from the spraying process.

#### 4. Conclusion

Low energy X-ray imaging is a highly effective tool for the rapid and non-destructive characterization of large scale gas diffusion electrodes for fuel cells. Calibration of the grayscale images can be implemented to allow for catalyst loading determination and platinum distribution mapping across the electrode geometric area.

In addition, the resolution of the technique is sufficient in observing artifacts that may have resulted from the spraying process. This approach, being simple in its design, has proved to be a vital tool in the study of electrode performance, development of new catalyst deposition processes and quality control for high-volume production.

#### Acknowledgments

We gratefully acknowledge financial support from the Danish Energy Agency, energinet.dk, the Danish Strategic Research Council, the Fuel Cells and Hydrogen joint undertaking (FCH-JU), and the Danish Advanced Technology Foundation.

#### References

- [1] J.S. Wainright, *J. Electrochem. Soc.* 142 (1995) L121.
- [2] R.A. Lemons, *J. Power Sources* 29 (1990) 251.
- [3] Q. Li, J.O. Jensen, R.F. Savinell, N.J. Bjerrum, *Prog. Polym. Sci.* 34 (2009) 449.
- [4] J.R. Varcoe, R.C.T. Slade, *Fuel Cells* 5 (2005) 187.
- [5] V. Mehta, J.S. Cooper, *J. Power Sources* 114 (2003) 32.
- [6] H.A. Gasteiger, S.S. Kocha, B. Sompalli, F.T. Wagner, *Appl. Catal. B Environ.* 56 (2005) 9.
- [7] W.K. Epting, J. Gelb, S. Litster, *Adv. Funct. Mater.* 22 (2012) 555.
- [8] H.-R. Jhong, F.R. Brushett, L. Yin, D.M. Stevenson, P.J.A. Kenis, *J. Electrochem. Soc.* 159 (2012) B292.
- [9] B. Bozzini, M.K. Abyaneh, M. Amati, A. Gianoncelli, L. Gregoratti, B. Kaulich, M. Kiskinova, *Chemistry* 18 (2012) 10196.
- [10] T. Arlt, I. Manke, K. Wippermann, H. Riesemeier, J. Mergel, J. Banhart, *J. Power Sources* 221 (2013) 210.
- [11] B. Bozzini, A. Gianoncelli, B. Kaulich, C. Mele, M. Prasciolu, M. Kiskinova, *Fuel Cells* 13 (2013) 196.
- [12] A. Pfrang, S. Didas, G. Tsotridis, *J. Power Sources* 235 (2013) 81.
- [13] S. Litster, W.K. Epting, E.A. Wargo, S.R. Kalidindi, E.C. Kumbur, *Fuel Cells* 13 (2013) n/a.
- [14] A. Diedrichs, M. Rastedt, F.J. Pinar, P. Wagner, *J. Appl. Electrochem.* 43 (2013) 1079.
- [15] T. Arlt, W. Maier, C. Tötze, C. Wannek, H. Markötter, F. Wieder, J. Banhart, W. Lehnert, I. Manke, *J. Power Sources* 246 (2014) 290.
- [16] R. Savinell, E. Yeager, D. Tryk, *J. Electrochem. Soc.* 141 (1994) 46.
- [17] L. Qingfeng, H.A. Hjuler, N.J. Bjerrum, *Electrochim. Acta* 45 (2000) 4219.